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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

003277-031

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.5)

10/018088

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371INTERNATIONAL APPLICATION NO.  
PCT/FI00/00532INTERNATIONAL FILING DATE  
14 June 2000PRIORITY DATE CLAIMED  
15 June 1999

## TITLE OF INVENTION

METHOD TO IMPROVE THE OPACITY OF MECHANICAL PULP BY USING ALIPHATIC PEROXY ACIDS AND USE OF PEROXY ACIDS TO IMPROVE OPACITY

## APPLICANT(S) FOR DO/EO/US

1) Jukka JÄKÄRÄ; and 2) Aarto PARÉN

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1.  This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2.  This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3.  This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4.  The US has been elected by the expiration of 19 months from the priority date (Article 31).
5.  A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a.  is attached hereto (required only if not communicated by the International Bureau).
  - b.  has been communicated by the International Bureau.
  - c.  is not required, as the application was filed in the United States Receiving Office (RO/US).
6.  An English language translation of the International Application as filed (35 U.S.C. 371(c)(2))
  - a.  is attached hereto.
  - b.  has been previously submitted under 35 U.S.C. 154(d)(4).
7.  Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a.  are attached hereto (required only if not communicated by the International Bureau).
  - b.  have been communicated by the International Bureau.
  - c.  have not been made; however, the time limit for making such amendments has NOT expired.
  - d.  have not been made and will not be made.
8.  An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9.  An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10.  An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

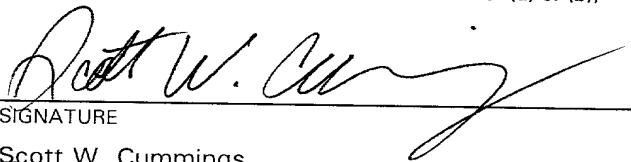
## Items 11 to 20 below concern document(s) or information included:

11.  An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12.  An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13.  A **FIRST** preliminary amendment.
14.  A **SECOND** or **SUBSEQUENT** preliminary amendment.
15.  A substitute specification.
16.  A change of power of attorney and/or address letter.
17.  A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18.  A second copy of the published international application under 35 U.S.C. 154(d)(4).
19.  A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20.  Other items or information:

International Search Report, International Preliminary Examination Report, Written Opinion, Form PCT/IB/304, PCT/IB/308, and Marked-up copy of Substitute Specification



21839

U.S. APPLICATION NO (If known, see 37 CFR 1.16)		INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
<b>10/018088</b>		PCT/FI00/00532	003277-031
21. <input checked="" type="checkbox"/> The following fees are submitted:		CALCULATIONS	PTO USE ONLY
<b>Basic National Fee (37 CFR 1.492(a)(1)-(5)):</b>			
<ul style="list-style-type: none"> <li>Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO . . . . . \$1,040.00 (960)</li> <li>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO . . . . . \$890.00 (970)</li> <li>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . . \$740.00 (958)</li> <li>International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . . \$710.00 (956)</li> <li>International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . . \$100.00 (962)</li> </ul>			
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>		\$ 1,040.00	
Surcharge of <b>\$130.00 (154)</b> for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492(e)).		20 <input type="checkbox"/> 30 <input type="checkbox"/>	\$ --
Claims	Number Filed	Number Extra	Rate
Total Claims	9 -20 =	0	X \$18.00 (966) \$ 0.00
Independent Claims	2 -3 =	0	X \$84.00 (964) \$ 0.00
Multiple dependent claim(s) (if applicable)			+ \$280.00 (968) \$ --
<b>TOTAL OF ABOVE CALCULATIONS =</b>		\$ 1,040.00	
Reduction for 1/2 for filing by small entity, if applicable (see below).		+ \$ --	
		<b>SUBTOTAL =</b>	\$ 1,040.00
Processing fee of <b>\$130.00 (156)</b> for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492(f)).		20 <input type="checkbox"/> 30 <input type="checkbox"/>	\$ --
		+ \$ --	
<b>TOTAL NATIONAL FEE =</b>		\$ 1,040.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 (581) per property		+ \$ --	
		+ \$ --	
<b>TOTAL FEES ENCLOSED =</b>		\$ 1,040.00	
		Amount to be refunded: \$ --	
		charged: \$ --	
a. <input type="checkbox"/> Small entity status is hereby claimed.			
b. <input checked="" type="checkbox"/> A check in the amount of <u>\$ 1,040.00</u> to cover the above fees is enclosed.			
c. <input type="checkbox"/> Please charge my Deposit Account No. 02-4800 in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.			
d. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-4800. A duplicate copy of this sheet is enclosed.			
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.			
SEND ALL CORRESPONDENCE TO:			
Ronald L. Grudziecki BURNS, DOANE, SWECKER & MATHIS, L.L.P. P.O. Box 1404 Alexandria, Virginia 22313-1404 (703) 836-6620			
		SIGNATURE	
Scott W. Cummings		NAME	
41,567		REGISTRATION NUMBER	
December 14, 2001		DATE	

10/018688  
14 Dec 2001

Patent  
Attorney's Docket No. 003277-031

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of ) **BOX PCT/US**  
                                  )  
Jukka JÄKÄRÄ et al.        )  
                                  )  
Application No.: [Not Assigned]        )  
International Application PCT/FI00/00532    )  
                                  )  
I.A. Date: June 14, 2000        )  
                                  )  
For:    METHOD TO IMPROVE THE        )  
        OPACITY OF MECHANICAL PULP    )  
        BY USING ALIPHATIC PEROXY    )  
        ACIDS AND USE OF PEROXY    )  
        ACIDS TO IMPROVE OPACITY    )

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to examination of the above-identified application on the merits, please amend the application as follows.

**IN THE SPECIFICATION:**

After the last page of the specification, please add the Abstract attached hereto as a separate sheet.

Also, please enter the attached Substitute Specification pursuant to 37 C.F.R.

§1.125.

**IN THE CLAIMS:**

*Please replace claims 1-9 with the corresponding amended claims.*

1. (Amended) A method for treating mechanical pulp, comprising adding an aliphatic percarboxylic acid to the pulp, in the amount of 0.5-5 kg/ton of pulp, to affect the opacity.
2. (Amended) The method according to Claim 1, wherein the amount of aliphatic percarboxylic acid that is added is 1-3 kg/ton of pulp.
3. (Amended) The method according to Claim 1, wherein the aliphatic percarboxylic acid is selected from among performic acid, peracetic acid or perpropionic acid.
4. (Amended) The method according to Claim 1, wherein the aliphatic percarboxylic acid is distilled or equilibrated peracetic acid.
5. (Amended) The method according to Claim 1, wherein the aliphatic percarboxylic acid is added to the pulp in connection with or after bleaching.
6. (Amended) The method according to Claim 5, wherein the pulp has been bleached with hydrogen peroxide and/or dithionite.

7. (Amended) The method according to Claim 1, wherein the aliphatic percarboxylic acid is added at a pulp consistency of 1-40%.

8. (Amended) The method according to Claim 1, wherein a mixture of aliphatic percarboxylic acid and Caro's acid is added to the pulp.

9. (Amended) A method of using aliphatic percarboxylic acid, comprising adding the acid to a mechanical pulp to improve opacity, in which the amount of percarboxylic acid is 0.5-5 kg/ton of pulp.

*Please cancel claim 10 without prejudice or disclaimer.*

**REMARKS**

By way of the foregoing amendments, the specification and claims have been amended to place them in better form for examination. No new matter has been added.

A Substitute Specification is being submitted to make minor changes. No new matter has been introduced.

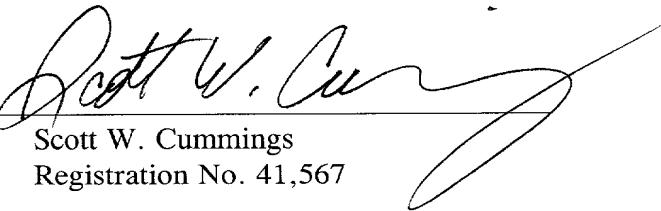
Also enclosed is a version of the Substitute Specification in which the amendments are shown with bracketing and underlining.

Early and favorable consideration with respect to this application is respectfully requested. Should any questions arise in connection with this application, the undersigned respectfully requests that he be contacted at the number indicated below.

Respectfully submitted,

BURNS, DOANE, SWECKER & MATHIS, L.L.P.

By:

  
Scott W. Cummings  
Registration No. 41,567

P.O. Box 1404  
Alexandria, Virginia 22313-1404  
(703) 836-6620

Date: December 14, 2001

**Attachment to Preliminary Amendment dated December 14, 2001**

**Marked-up Claims 1-9**

1. (Amended) A method for treating mechanical pulp, [characterized in that] comprising adding an aliphatic percarboxylic acid [is added] to the pulp, in the amount of 0.5-5 kg/ton of pulp, to affect the opacity.
  
2. (Amended) [A] The method according to Claim 1, wherein [characterized in that] the amount of aliphatic percarboxylic acid that is added is 1-3 kg/ton of pulp.
  
3. (Amended) [A] The method according to Claim 1, wherein [or 2, characterized in that] the aliphatic percarboxylic acid is selected from among performic acid, peracetic acid or perpropionic acid.
  
4. (Amended) [A] The method according to Claim 1, wherein [any of the preceding Claims, characterized in that] the aliphatic percarboxylic acid is distilled or equilibrated peracetic acid.
  
5. (Amended) [A] The method according to Claim 1, wherein [characterized in that] the aliphatic percarboxylic acid is added to the pulp in connection with or after bleaching.

**Attachment to Preliminary Amendment dated December 14, 2001**

**Marked-up Claims 1-9**

6. (Amended) [A] The method according to Claim 5, wherein [characterized in that] the pulp has been bleached with hydrogen peroxide and/or dithionite.

7. (Amended) [A] The method according to Claim 1, wherein [or 5, characterized in that] the aliphatic percarboxylic acid is [typically] added at a pulp consistency of 1-40%.

8. (Amended) [A] The method according to Claim 1, wherein [characterized in that] a mixture of aliphatic percarboxylic acid and Caro's acid is added to the pulp.

9. (Amended) [The use of] A method of using aliphatic percarboxylic acid, comprising adding the acid to a [to improve the opacity of] mechanical pulp to improve opacity, in which the amount of percarboxylic acid is 0.5-5 kg/ton of pulp.

**METHOD TO IMPROVE THE OPACITY OF  
MECHANICAL PULP BY USING ALIPHATIC PEROXY  
ACIDS AND USE OF PEROXY ACIDS TO IMPROVE OPACITY**

**FIELD OF THE INVENTION**

**[0001]** The invention relates to a process for treating mechanical pulps, which can be used to affect the opacity of the pulp.

**BACKGROUND OF THE INVENTION**

**[0002]** In the description of the background of the present invention that follows reference is made to certain structures and methods, however, such references should not necessarily be construed as an admission that these structures and methods qualify as prior art under the applicable statutory provisions. Applicants reserve the right to demonstrate that any of the referenced subject matter does not constitute prior art with regard to the present invention.

**[0003]** The nontransparent aspect of paper is described by opacity, which, along with brightness, is an important property of pulp in paper manufacture. Almost invariably, however, the opacity of the pulp decreases when the brightness increases. At present, mechanical pulps (refiner mechanical pulp, groundwood pulp, and chemi-mechanical pulp) are more and more often bleached with hydrogen peroxide. Dithionite bleaching is also used either alone or together with peroxide bleaching, whereupon dithionite is either used as refiner bleaching or after-bleaching. In the peroxide bleaching of pulp, mechanical pulp in particular, the

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decrease of opacity is clearly detectable, while the dithionite bleaching does not necessarily decrease the opacity. Generally, the lighter the level of bleaching the pulp, the lower the opacity of the pulp. The appended Fig. 1 that shows a variation in the opacity of spruce TMP, when peroxide is used to bleach pulp to various degrees of brightness manifests this. In certain paper grades, opacity is an important property. If we want to advance peroxide bleaching at the expense of dithionite bleaching, it would be important to be able to optimize peroxide bleaching so that the opacity remains as high as possible while the brightness grows.

5 [0004] Generally, the chemicals used in the peroxide bleaching of mechanical pulps are hydrogen peroxide, lye (alkali), and waterglass. The purpose of the base is to increase the pH to a sufficiently high level, so that the hydrogen peroxide is dissociated producing perhydroxyl anions. The purpose of the waterglass is to stabilize the hydrogen peroxide bleaching.

10 [0005] It is well known that peracetic acid can be produced in situ, for example, from acetanhydride or TAED (tetra acetyl ethylene diamine) or some other corresponding activator. One disadvantage of TAED is its high price and that it is a solid substance. It would be necessary to disperse the TAED in water before adding it to the pulp, which makes it difficult to use. Furthermore, TAED contains nitrogen, which might constitute a problem for environmental protection.

15 20 Acetanhydride is relatively cheap, but it would cause odor nuisance and be an inconvenient substance from the point of view of industrial safety. In addition,

when fed into an alkaline bleaching solution (NaOH + H<sub>2</sub>O<sub>2</sub> + waterglass), it would readily cause silicate precipitate and consume the lye.

[0006] Paper manufacture aims at ever-higher brightness levels. The brightness of paper can be affected, for example, by treating the paper with coating agents containing, among other things, pigments, binding agents, and plasticizing agents (JP application 284598).

[0007] However, the use of several coating agents at the final stage of paper manufacture adds to the manufacturing costs.

[0008] The agent that affects the opacity of a technically useful pulp should be liquid and stable, and it should preferably have a suitable pH value, so that no silicate precipitate would form in the bleaching. Because of environmental matters, a nitrogen-free substance would provide an additional benefit. The additive of the bleaching should also be cost-effective for the paper manufacturers. Consequently, a substance should be found for pulp bleaching, which, to fulfill the conditions mentioned above, is a reasonable, commercial chemical that is easy to get and can be added to the pulp as early as at the bleaching stage. Furthermore, attention should also be paid to the other effects of the substance, such as applicability in plant conditions.

[0009] The use of peracetic acid in bleaching chemical pulps is disclosed by the published Japanese application JP 57-21591, for example. However, bleaching processes like this aim at removing the lignin from the pulp and, in this case, the purpose is in no way to adjust the opacity of the pulp.

[0010] Tappi publication, Vol. 48, No. 2 (2/1965), W.H. Rapson et al. Paper Bleaching – A New Process, pp. 65-72, discloses a method for bleaching paper by using peracetic acid, among others. However, this method does not aim at improving the opacity of pulp, but increasing the brightness. Furthermore, the disclosed method uses considerable amounts of peracetic acid, about 1.2 – 2.5% (i.e., 12-25kg/ton of pulp). Such a portion can dissolve a considerable amount of lignin etc. from the pulp, whereupon the paper manufacturing process can be severely disturbed. The publication also reveals that the technical performance of the method deviates from our invention.

[0011] The use of peracids as a biocide is also disclosed by publication Kemia, No. 3 (1995), Jyri Maunuksela, Mikrobiens torjunta peretikkahapolla (Microbe Prevention with Peracetic Acid), pp. 242-244. Such a method aims at destroying microbe populations in the paper machine only. It is self-evident that peracetic acid, which is known to be an effective biocide, prevents the functioning of microbes in the water circulation, if a sufficient amount is present. The method disclosed by the publication uses a so-called equilibrium peracetic acid that contains a considerable amount of free acetic acid and hydrogen peroxide. The acetic acid and hydrogen peroxide that come with the peracid can disturb the paper manufacturing process.

[0012] Bleaching methods based on peracetic acid have also been presented, aiming at improving the brightness of the pulp compared with normal bleaching methods. Such a method is presented, for example, by publication Pulp and Paper Magazine of Canada, Convention Issue, 1972, pp. 123-131, and by number 3/1968

of the same magazine in pages 51-60. The doses of peracid used by these methods are very high and, consequently, dissolve a considerable amount of lignin from the surfaces of the fibres. In addition, these methods aim at increasing the brightness of the pulp, i.e. at bleaching.

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## SUMMARY OF THE INVENTION

[0013] One purpose of this invention is to find a useful substance that is used in pulp bleaching and that affects the opacity, fulfilling the conditions mentioned above.

[0014] Surprisingly, we have now observed that, when a small portion of peracid is either added to the peroxide bleaching or with the purpose of finishing the peroxide bleaching, the opacity of pulp improves compared with pulp of a corresponding brightness level that is bleached with hydrogen peroxide alone. At the same time, we have observed that peracids scarcely increase the brightness.

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[0015] One difference between the treatments mentioned above and our invention in particular is that the peracid treatments implemented by the means disclosed by them fail to improve the opacity of the pulp; none of the publications mentioned above tried to achieve a considerable increase in the opacity either.

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[0016] According to one aspect, the present invention provides a method for treating mechanical pulp, comprising adding an aliphatic percarboxylic acid to the pulp, in the amount of 0.5-5 kg/ton of pulp, to affect the opacity.

BRIEF DESCRIPTION OF THE DRAWING FIGURE

[0017] Fig. 1 is a plot showing brightness vs. opacity when peroxide is used to bleach pulp.

DETAILED DESCRIPTION OF THE INVENTION

5 [0018] The invention relates to a method, in which the peracid is either added to the peroxide bleaching or, preferably, after the peroxide bleaching, either to the storage tower of the bleached pulp or, for example, among the machine pulp in the paper machine. Typically, the amount of peracid added to the pulp is about 1-3 kg/ton of pulp. Because of its small amount, the peracid does not dissolve the lignin or the like from the pulp, whereupon it does not disturb the paper manufacturing process. It is especially advantageous to use peracid solutions, which have been purified, so that they mainly contain the peracid in question and water only. In that case, the addition of peracid does not have a considerable effect on the pH value of the stock, and no extra COD gets into the process. The invention differs from the known methods based on peracid namely in that it does not aim at increasing the 15 brightness but growing the opacity. A matter worth noticing in particular is that the method differs from the known bleaching treatments also in that the peracid doses used are very small and the method tries to avoid the dissolution of organic matter from the fibres.

20 [0019] The method is not actually a bleaching method, and the chemicals used in the actual bleaching of the pulp have no effect whatsoever on the functioning of the invention. The pulp can be bleached with dithionite, peroxide, dithionite and

peroxide, or it can even be completely unbleached. Any chelation agents or other additives used in pulp manufacture have no effect on the functioning of the invention either.

[0020] The consistency of the pulp at the moment the peracid is added can be 1-40%; the temperature can be 20-100°C. Depending on the process, the pH of the stock can be 3-11, preferably 4-8. If the peracid is added to alkaline peroxide bleaching, an advantageous pH value is 9-11, however. A suitable reaction time for the peracid is 1-300 minutes depending on the process.

[0021] The method is well suited to the treatment of mechanical pulp, such as groundwood pulp (SGW, PGW) and refiner mechanical pulp (TMP), or to treat chemi-mechanical pulps (CTMP). The sort of wood used to manufacture the pulp has no importance to the functioning of the invention.

[0022] A suitable dose of peracid has been found to be 0.5-5 kg/ton of pulp, typically 1-3 kg/ton of pulp. The peracid used can be any peracid that reasonably dissolves in water. We have noticed that peracetic acid and perpropionic acid are preferable peracids, and especially preferable are the peroxide-free distillates that are prepared from the equilibrium solutions of these. The manufacturing method of peracid has no effect on the functioning of the invention. Peracid solutions that are either purified by distillation or some other method, or the equilibrium solutions of peracids can be used as peracid. Various mixtures of peracids are also usable. One modification of the invention can use a mixture of peracid and Caro's acid.

**Example 1**

[0023] CTMP pulp was bleached with peroxide in a normal manner. Peracids were added to the bleaching solution, the results are shown in Table 1.

**Table 1**

[0024] CTMP, bleaching solution: NaOH 24 kg + waterglass 20 kg +  $H_2O_2$  30 kg/ton of pulp, 70°C, consistency 30%, 120 min, chelated pulp, peracid added to the bleaching, PAA = peracetic, PPA = perpropionic acid

	<b>Dosage, kg/ton of pulp</b>	<b>Brightness, % ISO</b>	<b>Opacity</b>
None	-	78.4	64.9
PAA	2	79.1	67.2
PPA	2.2	78.3	70.7

[0025] The results show that, by using peracids, a distinctly higher opacity with the same brightness level is achieved than by using peroxide bleaching alone.

**Example 2**

[0026] Bleached CTMP pulp was treated with peracids, the results are shown in Table 2.

**[0027] Table 2**

Bleached CTMP

After-treatment

$t = 50^\circ C$ , 30 min, pH 7, consistency 5%

	Dosage, kg/ton of pulp	Brightness, % ISO	Opacity
None	-	65.9	71.5
PAA	2	66.6	74.1
PPA	2.2	65.8	74.3

The results show that an after-treatment has an obvious effect on the opacity.

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### Example 3

[0028] So-called machine pulp taken from the plant and containing 16% of softwood pulp, 64% of TMP pulp, and 20% of coated broke (the basic pulp mixture was softwood: TMP 20:80) was treated with peracetic acid. The softwood pulp was normal ECF sulphate pulp. The TMP had been bleached with dithionite. The results are shown in Table 3.

[0029] **Table 3**

Pulp mixture:

Machine pulp	Softwood pulp	16%
	TMP	64%
	Coated broke	20%

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30 min, 70°C, Cs 3.2%, (the test was conducted by using the water of the plant)

No.	PAA, kg/ton of pulp	pH	TOC, kg/ton of pulp	Brightness, % ISO	Opacity, %	Note!
0	0	5.0	10.4	71.9	91.3	Untreated
1	0	4.9	9.6	71.6	91.8	30 min, at 70°C
2	1	4.6	8.9	71.7	96.5	Distilled PAA
3	2	4.6	9.6	71.9	95.8	Distilled PAA
4	4	4.2	10.2	71.3	96.9	Distilled PAA
5	2	4.5	11.0	70.7	97.1	Equilibrium solution
6	1	5.0	9.5	71.6	93.7	Distilled PAA
7	2	4.9	10.3	71.5	94.4	Distilled PAA
8	2	5.0	10.1	68.8	93.4	Equilibrium solution

Distilled PAA = 38% of PAA, 1% of H<sub>2</sub>O<sub>2</sub>

Equilibrium solution = PAA 13%, acetic acid 22%, H<sub>2</sub>O<sub>2</sub> 15%

[0030] The results show that the opacity grew considerably because of the treatment with PAA. They also show that the equilibrium solution has an adverse effect on the brightness. The TOC values (total organic carbon) show that the treatment did not dissolve considerable amounts of organic matter from the fibres.

[0031] While the present invention has been described by reference to the above-mentioned embodiments, certain modifications and variations will be evident to those of ordinary skill in the art. Therefore, the present invention is limited only by the scope and spirit of the appended claims.

1/P61&gt;

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JC13 Rec'd PCT/PCT 14 DEC 2001

Method to improve the opacity of mechanical pulp by using aliphatic peroxyacids and use of peroxyacids to improve opacity.

The invention relates to a process for treating mechanical pulps, which can be used 5 to affect the opacity of the pulp.

The nontransparent aspect of paper is described by opacity, which, along with brightness, is an important property of pulp in paper manufacture. Almost invariably, however, the opacity of the pulp decreases when the brightness increases. At 10 present, mechanical pulps (refiner mechanical pulp, groundwood pulp, and chemical mechanical pulp) are more and more often bleached with hydrogen peroxide. Dithionite bleaching is also used either alone or together with peroxide bleaching, whereupon dithionite is either used as refiner bleaching or after-bleaching. In the peroxide bleaching of pulp, mechanical pulp in particular, the decrease of opacity is clearly detectable, while the dithionite bleaching does not necessarily decrease the 15 opacity. Generally, the lighter the level of bleaching the pulp, the lower the opacity of the pulp. The appended Fig. 1 that shows a variation in the opacity of spruce TMP, when peroxide is used to bleach pulp to various degrees of brightness manifests this. In certain paper grades, opacity is an important property. If we want to 20 advance peroxide bleaching at the expense of dithionite bleaching, it would be important to be able to optimize peroxide bleaching so that the opacity remains as high as possible while the brightness grows.

Generally, the chemicals used in the peroxide bleaching of mechanical pulps are 25 hydrogen peroxide, lye (alkali), and waterglass. The purpose of the base is to increase the pH to a sufficiently high level, so that the hydrogen peroxide is dissociated producing perhydroxyl anions. The purpose of the waterglass is to stabilize the hydrogen peroxide bleaching.

It is well known that peracetic acid can be produced in situ, for example, from 30 acetanhydride or TAED (tetra acetyl ethylene diamine) or some other corresponding activator. One disadvantage of TAED is its high price and that it is a solid substance. It would be necessary to disperse the TAED in water before adding it to the pulp, which makes it difficult to use. Furthermore, TAED contains nitrogen, which 35 might constitute a problem for environmental protection. Acetanhydride is relatively cheap, but it would cause odour nuisance and be an inconvenient substance from the point of view of industrial safety. In addition, when fed into an alkaline bleaching solution (NaOH + H<sub>2</sub>O<sub>2</sub> + waterglass), it would readily cause silicate precipitate and consume the lye.

Paper manufacture aims at ever-higher brightness levels. The brightness of paper can be affected, for example, by treating the paper with coating agents containing, among other things, pigments, binding agents, and plasticizing agents (JP application 284598).

5 However, the use of several coating agents at the final stage of paper manufacture adds to the manufacturing costs.

The agent that affects the opacity of a technically useful pulp should be liquid and stable, and it should preferably have a suitable pH value, so that no silicate precipitate would form in the bleaching. Because of environmental matters, a nitrogen-free 10 substance would provide an additional benefit. The additive of the bleaching should also be cost-effective for the paper manufacturers. Consequently, a substance should be found for pulp bleaching, which, to fulfil the conditions mentioned above, is a reasonable, commercial chemical that is easy to get and can be added to the pulp as early as at the bleaching stage. Furthermore, attention should also be paid to 15 the other effects of the substance, such as applicability in plant conditions.

The purpose of this invention is to find a useful substance that is used in pulp bleaching and that affects the opacity, fulfilling the conditions mentioned above.

The main features of the invention are disclosed by the appended Claims.

Surprisingly, we have now observed that, when a small portion of peracid is either 20 added to the peroxide bleaching or with the purpose of finishing the peroxide bleaching, the opacity of pulp improves compared with pulp of a corresponding brightness level that is bleached with hydrogen peroxide alone. At the same time, we have observed that peracids scarcely increase the brightness.

The use of peracetic acid in bleaching chemical pulps is disclosed by the published 25 Japanese application JP 57-21591, for example. However, bleaching processes like this aim at removing the lignin from the pulp and, in this case, the purpose is in no way to adjust the opacity of the pulp.

Tappi publication, Vol. 48, No. 2 (2/1965), W.H. Rapson et al. Paper Bleaching – A 30 New Process, pp. 65-72, discloses a method for bleaching paper by using peracetic acid, among others. However, this method does not aim at improving the opacity of pulp, but increasing the brightness. Furthermore, the disclosed method uses considerable amounts of peracetic acid, about 1.2 – 2.5% (i.e., 12-25kg/ton of pulp). Such a portion can dissolve a considerable amount of lignin etc. from the pulp, whereupon the paper manufacturing process can be severely disturbed. The publication 35 also reveals that the technical performance of the method deviates from our invention.

The use of peracids as a biocide is also disclosed by publication Kemia, No. 3 (1995), Jyri Maunuksela, Mikrobiens torjunta peretikkahapolla (Microbe Prevention with Peracetic Acid), pp. 242-244. Such a method aims at destroying microbe populations in the paper machine only. It is self-evident that peracetic acid, which is known to be an effective biocide, prevents the functioning of microbes in the water circulation, if a sufficient amount is present. The method disclosed by the publication uses a so-called equilibrium peracetic acid that contains a considerable amount of free acetic acid and hydrogen peroxide. The acetic acid and hydrogen peroxide that come with the peracid can disturb the paper manufacturing process.

10 Bleaching methods based on peracetic acid have also been presented, aiming at improving the brightness of the pulp compared with normal bleaching methods. Such a method is presented, for example, by publication Pulp and Paper Magazine of Canada, Convention Issue, 1972, pp. 123-131, and by number 3/1968 of the same magazine in pages 51-60. The doses of peracid used by these methods are very high and, consequently, dissolve a considerable amount of lignin from the surfaces of the fibres. In addition, these methods aim at increasing the brightness of the pulp, i.e. at bleaching.

15 One difference between the treatments mentioned above and our invention in particular is that the peracid treatments implemented by the means disclosed by them fail to improve the opacity of the pulp; none of the publications mentioned above tried to achieve a considerable increase in the opacity either.

20 The invention relates to a method, in which the peracid is either added to the peroxide bleaching or, preferably, after the peroxide bleaching, either to the storage tower of the bleached pulp or, for example, among the machine pulp in the paper machine.

25 Typically, the amount of peracid added to the pulp is about 1-3 kg/ton of pulp. Because of its small amount, the peracid does not dissolve the lignin or the like from the pulp, whereupon it does not disturb the paper manufacturing process. It is especially advantageous to use peracid solutions, which have been purified, so that they mainly contain the peracid in question and water only. In that case, the addition of peracid does not have a considerable effect on the pH value of the stock, and no extra COD gets into the process. The invention differs from the known methods based on peracid namely in that it does not aim at increasing the brightness but growing the opacity. A matter worth noticing in particular is that the method differs from the known bleaching treatments also in that the peracid doses used are very small and the method tries to avoid the dissolution of organic matter from the fibres.

30 The method is not actually a bleaching method, and the chemicals used in the actual bleaching of the pulp have no effect whatsoever on the functioning of the invention.

The pulp can be bleached with dithionite, peroxide, dithionite and peroxide, or it can even be completely unbleached. Any chelation agents or other additives used in pulp manufacture have no effect on the functioning of the invention either.

5 The consistency of the pulp at the moment the peracid is added can be 1-40%; the temperature can be 20-100°C. Depending on the process, the pH of the stock can be 3-11, preferably 4-8. If the peracid is added to alkaline peroxide bleaching, an advantageous pH value is 9-11, however. A suitable reaction time for the peracid is 1-300 minutes depending on the process.

10 The method is well suited to the treatment of mechanical pulp, such as groundwood pulp (SGW, PGW) and refiner mechanical pulp (TMP), or to treat chemi-mechanical pulps (CTMP). The sort of wood used to manufacture the pulp has no importance to the functioning of the invention.

15 A suitable dose of peracid has been found to be 0.5-5 kg/ton of pulp, typically 1-3 kg/ton of pulp. The peracid used can be any peracid that reasonably dissolves in water. We have noticed that peracetic acid and perpropionic acid are preferable peracids, and especially preferable are the peroxide-free distillates that are prepared from the equilibrium solutions of these. The manufacturing method of peracid has no effect on the functioning of the invention. Peracid solutions that are either purified by distillation or some other method, or the equilibrium solutions of peracids can be used as peracid. Various mixtures of peracids are also usable. One modification of the invention can use a mixture of peracid and Caro's acid.

#### Example 1

CTMP pulp was bleached with peroxide in a normal manner. Peracids were added to the bleaching solution, the results are shown in Table 1.

25 Table 1

CTMP, bleaching solution: NaOH 24 kg +waterglass 20 kg + H<sub>2</sub>O<sub>2</sub> 30 kg/ton of pulp, 70°C, consistency 30%, 120 min, chelated pulp, peracid added to the bleaching, PAA = peracetic, PPA = perpropionic acid

	Dosage, kg/ton of pulp	Brightness, % ISO	Opacity
None	-	78.4	64.9
PAA	2	79.1	67.2
PPA	2.2	78.3	70.7

30

The results show that, by using peracids, a distinctly higher opacity with the same brightness level is achieved than by using peroxide bleaching alone.

**Example 2**

Bleached CTMP pulp was treated with peracids, the results are shown in Table 2.

**Table 1**

Bleached CTMP

5 **After-treatment**

$t = 50^{\circ}\text{C}$ , 30 min, pH 7, consistency 5%

	Dosage, kg/ton of pulp	Brightness, % ISO	Opacity
None	-	65.9	71.5
PAA	2	66.6	74.1
PPA	2.2	65.8	74.3

The results show that an after-treatment has an obvious effect on the opacity.

**Example 3**

10 So-called machine pulp taken from the plant and containing 16% of softwood pulp, 64% of TMP pulp, and 20% of coated broke (the basic pulp mixture was softwood: TMP 20:80) was treated with peracetic acid. The softwood pulp was normal ECF sulphate pulp. The TMP had been bleached with dithionite. The results are shown in Table 3.

15 **Table 3**

Pulp mixture:

Machine pulp	Softwood pulp	16%
	TMP	64%
	Coated broke	20%

30 min, 70°C, Cs 3.2%, (the test was conducted by using the water of the plant)						
No.	PAA, kg/ton of pulp	pH	TOC, kg/ton of pulp	Brightness, % ISO	Opacity, %	Note!
0	0	5.0	10.4	71.9	91.3	Untreated
1	0	4.9	9.6	71.6	91.8	30 min, at 70°C
2	1	4.6	8.9	71.7	96.5	Distilled PAA
3	2	4.6	9.6	71.9	95.8	Distilled PAA
4	4	4.2	10.2	71.3	96.9	Distilled PAA
5	2	4.5	11.0	70.7	97.1	Equilibrium solution
6	1	5.0	9.5	71.6	93.7	Distilled PAA
7	2	4.9	10.3	71.5	94.4	Distilled PAA
8	2	5.0	10.1	68.8	93.4	Equilibrium solution

20 Distilled PAA = 38% of PAA, 1% of  $\text{H}_2\text{O}_2$

Equilibrium solution = PAA 13%, acetic acid 22%,  $\text{H}_2\text{O}_2$  15%

The results show that the opacity grew considerably because of the treatment with PAA. They also show that the equilibrium solution has an adverse effect on the brightness. The TOC values (total organic carbon) show that the treatment did not dissolve considerable amounts of organic matter from the fibres.

**Amended claims**

1. A method for treating mechanical pulp, **characterized** in that an aliphatic percarboxylic acid is added to the pulp, in the amount of 0.5 – 5 kg/ton of pulp, to affect the opacity.
2. A method according to Claim 1, **characterized** in that the amount of aliphatic percarboxylic acid that is added is 1 – 3 kg/ton of pulp.
3. A method according to Claim 1 or 2, **characterized** in that the aliphatic percarboxylic acid is selected from among performic acid, peracetic acid or perpropionic acid.
4. A method according to any of the preceding Claims, **characterized** in that the aliphatic percarboxylic acid is distilled or equilibrated peracetic acid.
5. A method according to Claim 1, **characterized** in that the aliphatic percarboxylic acid is added to the pulp in connection with or after bleaching.
6. A method according to Claim 5, **characterized** in that the pulp has been bleached with hydrogen peroxide and/or dithionite.
7. A method according to Claim 1 or 5, **characterized** in that the aliphatic percarboxylic acid is typically added at a pulp consistency of 1 – 40%.
8. A method according to Claim 1, **characterized** in that a mixture of aliphatic percarboxylic acid and Caro's acid is added to the pulp.
9. The use of aliphatic percarboxylic acid to improve the opacity of mechanical pulp, in which the amount of percarboxylic acid is 0.5 – 5 kg/ton of pulp.

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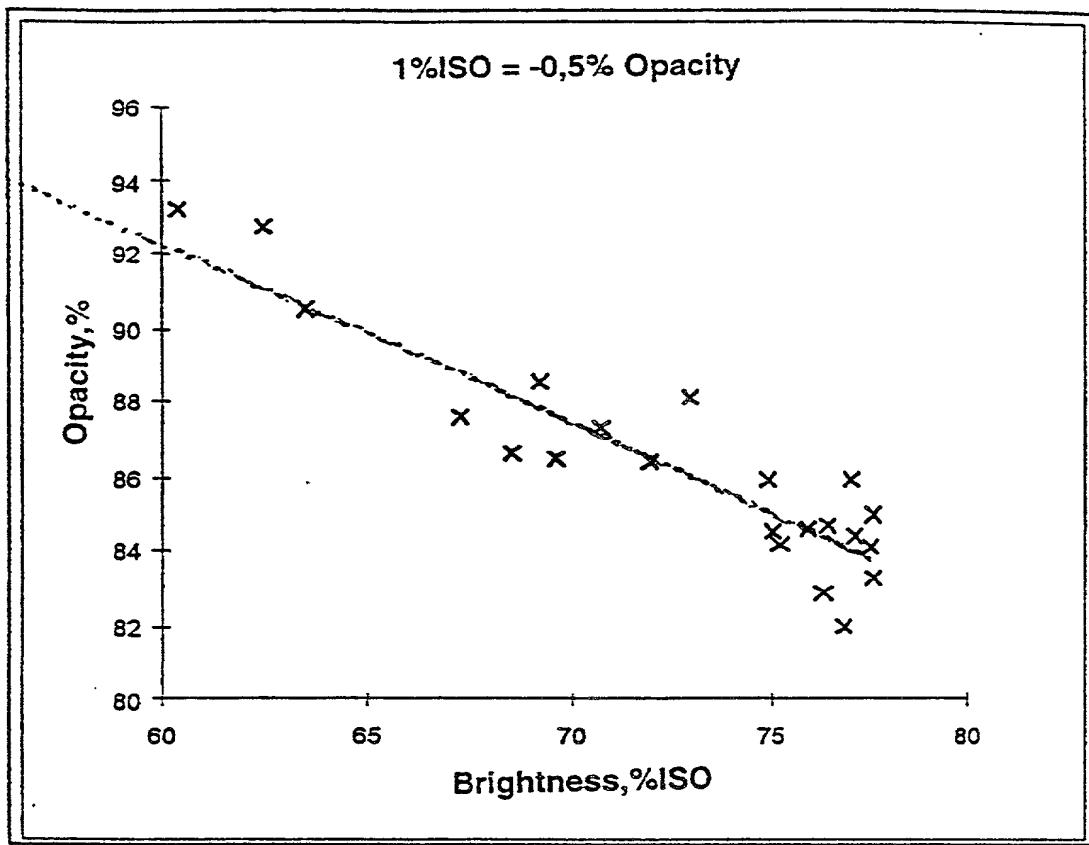


Fig. 1

**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY**  
 (Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;  
 I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: **METHOD TO IMPROVE THE OPACITY OF MECHANICAL PULP BY USING ALIPHATIC PEROXYACIDS AND USE OF PEROXYACIDS TO IMPROVE OPACITY**

the specification of which (check only one item below):

is attached hereto.  
 was filed as United States application

Number \_\_\_\_\_  
 on \_\_\_\_\_  
 and was amended  
 on \_\_\_\_\_ (if applicable).

was filed as PCT international application

Number PCT/FI00/00532  
 on 14 June 2000  
 and was amended  
 on 2 July 2001 (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(e) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

**PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. §119:**

COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 U.S.C. §119
Finland	991366	15 June 1999	<u>X</u> Yes <u>  </u> No
PCT	PCT/FI00/00532	14 June 2000	<u>X</u> Yes <u>  </u> No
			<u>  </u> Yes <u>  </u> No
			<u>  </u> Yes <u>  </u> No
			<u>  </u> Yes <u>  </u> No

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

\_\_\_\_\_ (Application Number)

\_\_\_\_\_ (Filing Date)

\_\_\_\_\_ (Application Number)

\_\_\_\_\_ (Filing Date)

**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONT'D)**  
(Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

I hereby claim the benefit under Title 35, United States Code, §120 of any United States applications(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose to the Office all information known to me to be material to the patentability as defined in Title 37, Code of Federal Regulations §1.56, which became available between the filing date of the prior application(s) and the national or PCT international filing date of this application:

**PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. §120:**

<b>U.S. APPLICATIONS</b>		<b>STATUS (check one)</b>		
<b>U.S. APPLICATION NUMBER</b>	<b>U.S. FILING DATE</b>	<b>PATENTED</b>	<b>PENDING</b>	<b>ABANDONED</b>
<b>PCT APPLICATIONS DESIGNATING THE U.S.</b>				
<b>PCT APPLICATION NO.</b>	<b>PCT FILING DATE</b>	<b>U.S. APPLICATION NUMBERS ASSIGNED (if any)</b>		

I hereby appoint the following attorneys and agent(s) to prosecute said application and to transact all business in the Patent and Trademark Office connected therewith and to file, prosecute and to transact all business in connection with international applications directed to said invention:

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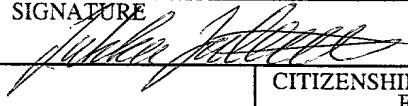
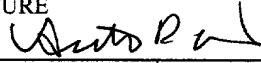
**21839**

Address all telephone calls to: \_\_\_\_\_ Ronald L. Grudziecki \_\_\_\_\_ at (703) 836-6620.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONT'D)  
(Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

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RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SEVENTH JOINT INVENTOR, IF ANY		SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF EIGHTH JOINT INVENTOR, IF ANY		SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			